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(54) COMPOSITION FOR PRODUCING PRECOATED STEEL SHEET

(57)Abstract:

PURPOSE: To obtain a composition for a precoated steel sheet having a high curing rate and giving a cured film excellent in hardness, impact resistance, adhesion to steel sheet and bendability by mixing a compound having oxetane rings with a cationic photopolymerization initiator.

CONSTITUTION: This composition is obtained by mixing a compound (A) having 1-4 oxetane rings with an epoxy compound (B), a compound (C) having a vinyl ether group or a compound (D) having a (meth)acryloyl group (D) as an optional component and a radical photopolymerization initiator in a weight ratio (B to D)/(A to D) of (5-95)/100, and adding 0.1-20wt.%, based on the total of components A to C, a cationic photopolymerization initiator. The radical photopolymerization initiator is used in an amount of 0.01-20wt.% based on component D. This composition is applied to the surface of a steel sheet and cured by irradiation with an actinic radiation to obtain a precoated steel sheet.

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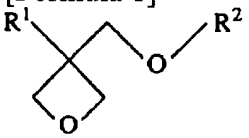
* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the constituent for precoat steel plate manufacture which consists of a compound which has an oxetane ring. In addition, in this specification, an acryloyl radical or a methacryloyl radical is expressed as an acryloyl (meta) radical.
[0002]
[Description of the Prior Art] In recent years, in the home electrical and electric equipment, interior building materials, an office machine, or a car manufacturer, for the reasons of pollution-free, reduction of labor, process saving, etc., the postcoat which paints after processing it is avoided and it is processed more often using a precoat steel plate. However, the conventional precoat steel plate has about the same degree of hardness as a postcoat, and shock resistance, and there was no high workability, for example, the thing which bends 0T and can be equal to processing. Therefore, when adopting a precoat steel plate as a specific field with the above manufacturers, the present condition is sacrificing either of said properties. For example, what used heat-curing hard acrylic paint material is lacking in workability.
[0003] By the way, since an activity energy-line hardening technique has various good properties, such as work environment of the quick cure rate and the non-stain resistance by generally being a non-solvent, and the very low energy amount required, it is becoming very important in various industries, such as an ornament of coating of wood, and a metal, and printing. The early development in this field is concentrated on activity energy-line initiation radical polymerizations, such as polyfunctional acrylate and unsaturated polyester, and these ingredients are still used in large quantities even today. Also in current, although most of these researches are turned to the activity energy-line initiation radical polymerization, activity energy-line initiation being also ionic polymerization and being also quite promising in many applicable fields are fully admitted. There is no limit that especially activity energy-line initiation cationic polymerization must be carried out especially under an inert atmosphere since a polymerization is not checked by oxygen, and it has the advantage that a prompt and perfect polymerization can be performed in air. Development of an activity energy-line initiation cationic polymerization technique was concentrated on two kinds of monomers called an epoxy resin and vinyl ether till today. Especially a photoresist epoxy resin is excellent in an adhesive property, and the paint film has thermal resistance and good chemical resistance. However, in the conventional photoresist epoxy resin, since it had the defect in which a photopolymerization rate is comparatively slow, it was not able to be used in the application asked for prompt photo-curing. Moreover, toxicity including mutation is pointed out and, as for the photoresist epoxy resin of low molecular weight, the danger is regarded as questionable. There is much what has an odor strong in on the other hand photoresist vinyl ether being volatile, and there is much what the contraction at the time of hardening is accepted in as compared with photoresist epoxy. Adhesion may be spoiled by the contraction at the time of hardening in manufacture of the precoat steel plate which cannot expect improvement in the adhesion by the graft reaction with the sink phenomenon to a base material, or a base material especially.
[0004]

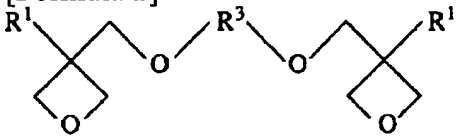
[Problem(s) to be Solved by the Invention] As a constituent used for manufacture of a precoat steel plate, although said epoxy resin and vinyl ether were examined, when an epoxy resin was used as mentioned above, the problem was in hardenability and toxicity, and when another side vinyl ether was used, contraction was caused at the time of volatility, the problem of an odor, and hardening, and it had the problem which says **** to adhesion with a steel plate. In view of the above-mentioned situation, there was no toxicity etc., this invention persons had the quick cure rate, and the hardening film was excellent in a degree of hardness, shock resistance, adhesion with a steel plate, etc., and in order that a crack did not arise by bending, i.e., they might find out the constituent for precoat steel plate manufacture which bends 0T and is excellent in workability, they inquired wholeheartedly.
[0005]
[Means for Solving the Problem] this invention persons completed header this invention for the ability of the constituent which consists of cyclic ether which has specific structure by various examination to solve the above-mentioned technical problem as a constituent for precoat steel plate manufacture. Namely, the constituent for precoat steel plate manufacture which consists of a compound with which the 1st invention of this invention has 1-4 oxetane rings, and an optical cationic initiator, The constituent for precoat steel plate manufacture of the 1st invention which contains further the compound with which the 2nd invention has an epoxy group, The constituent for precoat steel plate manufacture of the 1st invention which contains further the compound with which the 3rd invention has a vinyl ether radical, The constituent for precoat steel plate manufacture of the 1st invention which contains further the compound with which the 4th invention has an acryloyl (meta) radical, and an optical radical polymerization initiator, It is the precoat steel plate with which the 6th invention has the hardening film of the constituent of the 1-4th invention on a steel plate front face in the manufacture approach of the precoat steel plate characterized by for the 5th invention applying the constituent of the 1-4th invention to a steel plate front face, and making it harden it by the exposure of an activity energy line, and a list. Hereafter, this invention is explained to a detail.
[0006] O The compound which has the oxetane ring used by compound this invention which has 1-4 oxetane rings has 1-4 oxetane rings. When the compound which has five or more oxetane rings is used, flexibility is lost by the hardening film of a constituent and the precoat steel plate obtained may cause a cracking crack by bending. Various things can be used for it if the compound which has the oxetane ring used by this invention is a compound which has 1-4 oxetane rings. As a compound which has one oxetane ring, the compound specifically shown by the following general formula (1) is mentioned.
[0007]
[Formula 1]



(1)

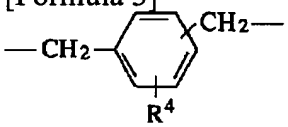
[0008] It sets at a ceremony (1) and is R1. They are the alkyl group of 1-6 carbon numbers, such as a hydrogen atom, a methyl group, an ethyl group, a propyl group, or butyl, the fluoro alkyl group of 1-6 carbon numbers, an allyl group, an aryl group, a furil radical, or a thienyl group. R2 The alkyl group of 1-6 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or butyl, 1-propenyl radical, 2-propenyl radical, a 2-methyl-1-propenyl radical, The alkenyl radical of 2-6 carbon numbers, such as a 2-methyl-2-propenyl radical, 1-butenyl group, 2-butenyl group, or 3-butenyl group, The radical which has rings, such as a phenyl group, benzyl, fluoro benzyl, a methoxybenzyl radical, or a phenoxy ethyl group, The alkyl carbonyl group of 2-6 carbon numbers, such as an ethyl carbonyl group, a propylcarbonyl radical, or a butyl carbonyl group, The alkoxy carbonyl group of 2-6 carbon numbers, such as an ethoxycarbonyl radical, a propoxy carbonyl group, or a butoxycarbonyl radical, Or it is N-alkyl carbamoyl group of 2-6 carbon numbers, such as an ethyl carbamoyl group, a propyl carbamoyl group, a butylcarbamoyl radical, or a pentyl carbamoyl group, etc.
[0009] Next, as a compound which has two oxetane rings, the compound shown by the following

general formula (2) is listed.
[0010]
[Formula 2]



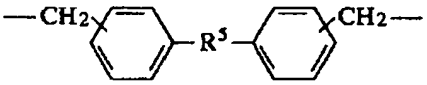
(2)

[0011] It sets at a ceremony (2) and is R1. It is the same radical as the thing in said general formula (1). R3 For example, they are the alkylene group containing lines, such as lines, such as lines, such as ethylene, a propylene radical, or a butylene radical, or a branching-like alkylene group, a poly (ethyleneoxy) group, or the Pori (propyleneoxy) radical, or a branching-like Pori (alkyleneoxy) radical, a pro PENIREN radical, a methyl pro PENIREN radical, or a butenylene radical, or a branching-like unsaturated hydrocarbon radical, a carbonyl group, and a carbonyl group, an alkylene group containing a carboxyl group, or an alkylene group containing a carbamoyl group. Moreover, R3 It is also the polyad chosen from the radical shown by the following type (3), (4), and (5).
[0012]
[Formula 3]



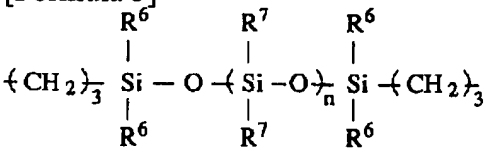
(3)

[0013] It sets at a ceremony (3) and is R4. The alkyl group of 1-4 carbon numbers, such as a hydrogen atom, a methyl group, an ethyl group, a propyl group, or butyl, They are halogen atoms, such as an alkoxy group of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, or a butoxy radical, a chlorine atom, or a bromine atom, a nitro group, a cyano group, a sulfhydryl group, a low-grade alkyl carboxyl group, a carboxyl group, or a carbamoyl group.
[0014]
[Formula 4]



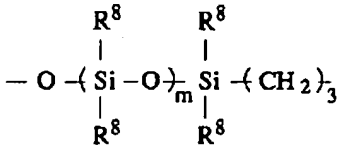
(4)

[0015] a formula (4) -- setting -- R5 An oxygen atom, a sulfur atom, a methylene group, NH, SO and SO2, and C (CF3)2 Or C(CH3) 2 it is .
[0016]
[Formula 5]



(5)

[0017] It sets at a ceremony (5) and is R6. They are the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or butyl, or an aryl group. It is the integer of 0-2000, as for n, it is desirable that n is 0-6 when high surface hardness is required of the hardening film of a constituent, and when high tensile strength is required of the hardening film of a constituent, it is desirable that n is 100-200. R7 They are the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or butyl, or an aryl group. R7 It is also the polyad chosen from the radical shown by the following formula (6).
[0018]
[Formula 6]

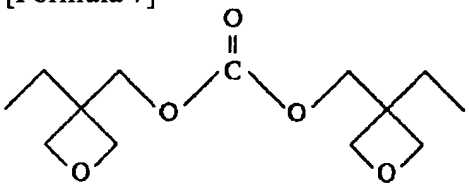


(6)

[0019] It sets at a ceremony (6) and is R8. They are the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, and butyl, or an aryl group. m is the integer of 0-100. As an example of a compound of having two oxetane rings, the compound shown by the following formula (7) and (8) is mentioned.

[0020]

[Formula 7]

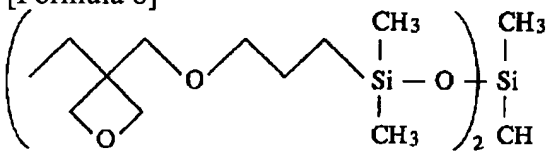


(7)

[0021] It sets at a ceremony (2) and the compound shown by the formula (7) is R1. An ethyl group and R3 It is the compound which is a carboxyl group.

[0022]

[Formula 8]



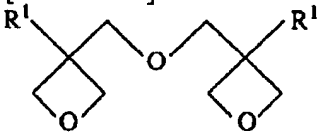
(8)

[0023] It sets to a general formula (2) and the compound shown by the formula (8) is R1. An ethyl group and R3 are R6 at a formula (5). And R7 They are a methyl group and the compound whose n is 1.

[0024] In the compound which has two oxetane rings, there is a compound shown by the following general formula (9) as desirable examples other than the above-mentioned compound.

[0025]

[Formula 9]

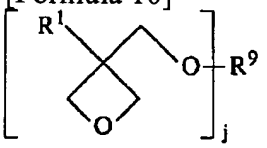


(9)

[0026] As a compound which has 3-4 oxetane rings, the compound shown by the following general formula (10) is mentioned.

[0027]

[Formula 10]



(10)

[0028] It sets at a ceremony (10) and is R1. It is the same radical as the thing in said general formula (1). R9 For example, the following type (11) Branching-like polysiloxy radicals, such as a radical shown by a branching-like Pori (alkyleneoxy) radical or the following formulas (15), such as a branching-like alkylene group of the carbon numbers 1-12, such as a radical shown by - (13), and a radical shown by the following formula (14), etc. mention, and it is ****. j is 3 or 4.

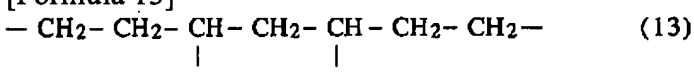
[0029]
[Formula 11]

(11)

[0030] In [type (11), R10 is low-grade alkyl groups, such as a methyl group, an ethyl group, or a propyl group.]
[0031]
[Formula 12]

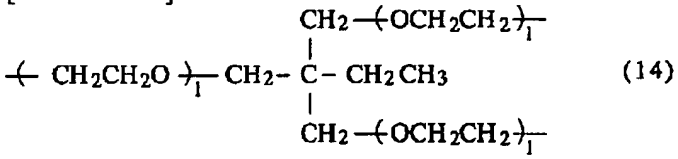
(12)

[0032]
[Formula 13]



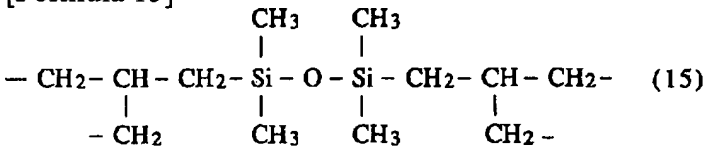
(13)

[0033]
[Formula 14]



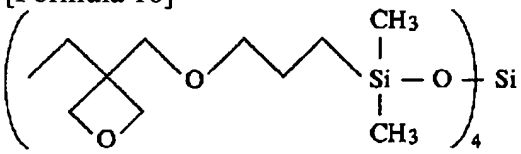
(14)

[0034] In [type (14), l is the integer of 1-10.]
[0035]
[Formula 15]



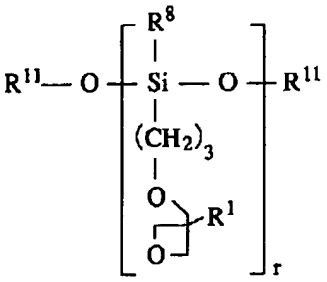
(15)

[0036] As an example of a compound of having 3-4 oxetane rings, the compound shown by the following formula (16) is mentioned.
[0037]
[Formula 16]



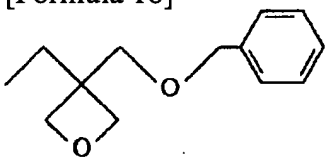
(16)

[0038] Furthermore, as an example of the compound which has 1-4 oxetane rings except having described above, there is a compound shown by the following formula (17).
[0039]
[Formula 17]



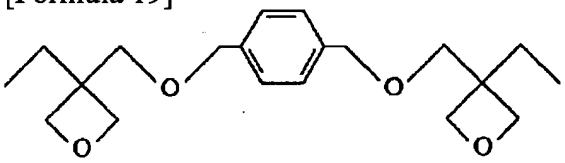
(17)

[0040] It sets at a ceremony (17) and is R8. It is the same radical as the thing in a formula (6). R11 is the alkyl group or trialkylsilyl groups of carbon numbers 1-4, such as a methyl group, an ethyl group, a propyl group, or butyl, and r is 1-4.
[0041] There is a compound shown below as a more desirable example of the oxetane compound used by this invention.
[0042]
[Formula 18]



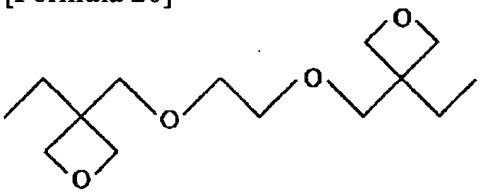
(18)

[0043]
[Formula 19]



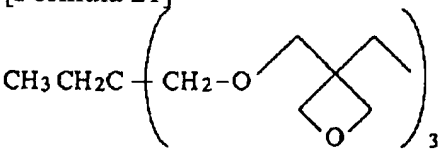
(19)

[0044]
[Formula 20]



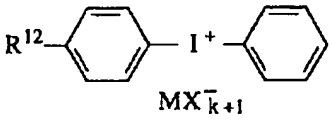
(20)

[0045]
[Formula 21]



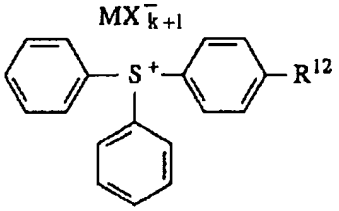
(21)

[0046] O Various things can be used as an optical cationic initiator used with the constituent of optical cationic initiator this invention. A diaryl iodonium salt and a triarylsulfonium salt are mentioned as a thing desirable as these initiators. A typical optical cationic initiator is shown below.
[0047]
[Formula 22]



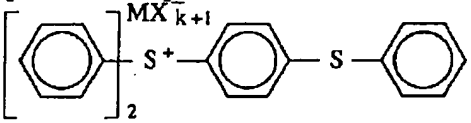
(22)

[0048]
[Formula 23]



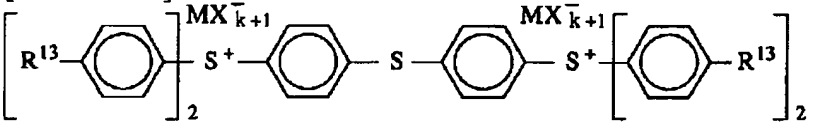
(23)

[0049]
[Formula 24]



(24)

[0050]
[Formula 25]



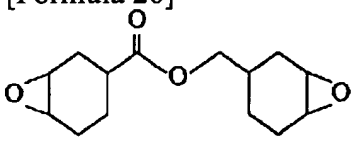
(25)

[0051] R12 is a hydrogen atom, the alkyl group of carbon numbers 1-18, or the alkoxy group of carbon numbers 1-18 among a formula, and R13 is a hydrogen atom, a hydroxyalkyl radical, and a hydroxy alkoxy group, and is a hydroxy ethoxy radical preferably. M -- a metal -- desirable -- antimony -- it is -- X -- a halogen -- it is a fluorine preferably, and k is a metaled valence, for example, in the case of antimony, it is 5. As for an optical cationic initiator, it is desirable to contain at 0.1 - 20% of the weight of a rate to the compound which has an oxetane ring, and it is 0.1 - 10 % of the weight more preferably. When making the constituent of the 1st invention which carries out a postscript contain the compound which has the compound and/or vinyl ether radical which have an epoxy group further, it is desirable to contain at 0.1 - 20% of the weight of a rate to the total quantity of the compound which has the compound which has an oxetane ring, the compound which has an epoxy group, and/or a vinyl ether radical, and it is 0.1 - 10 % of the weight more preferably. When not filling to 0.1% of the weight, hardenability becomes less enough, when exceeding another side and 20 % of the weight, light transmission nature becomes poor, uniform hardening may not be able to be performed or the smooth nature of a hardening film front face may be lost.
[0052] O Other components can be blended with the constituent of other compound this inventions if needed besides the above-mentioned indispensable component. The 2nd invention of this invention is a constituent for precoat steel plate manufacture containing the compound which has an epoxy group further in the constituent of the 1st invention. In this case, the cure rate of a constituent is further improvable by making an epoxy compound contain in a constituent. Various things can be used as a compound which has an epoxy group. For example, as an epoxy compound which has one epoxy group, there are phenyl glycidyl ether, butyl glycidyl ether, etc., and hexanediol diglycidyl ether, tetraethylene glycol diglycidyl ether, trimethylolpropane triglycidyl ether, bisphenol A diglycidyl ether, a novolak

mold epoxy compound, etc. are mentioned as an epoxy compound which has two or more epoxy groups. It is desirable especially to use an alicyclic epoxy compound by this invention, for example, the compound shown below is mentioned.

[0053]

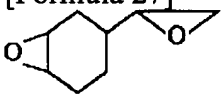
[Formula 26]



(26)

[0054]

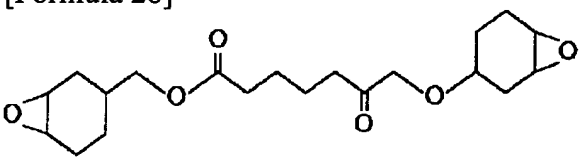
[Formula 27]



(27)

[0055]

[Formula 28]



(28)

[0056] In this case, as the blending ratio of coal of a compound which has an epoxy group, 5 - 95 weight section is desirable to the total quantity 100 weight section of the compound which has the 1-4 above-mentioned oxetane rings, and the compound which has an epoxy group.

[0057] The 3rd invention of this invention is a constituent for precoat steel plate manufacture containing the compound which has a vinyl ether radical further in the constituent of the 1st invention. In this case, the cure rate of a constituent is further improvable by making the compound which has a vinyl ether radical contain in a constituent. Various things can be used as a compound which has a vinyl ether radical. For example, as a compound which has one vinyl ether radical, hydroxyethyl vinyl ether, hydroxy butyl vinyl ether, dodecyl vinyl ether, propenyl ether propylene carbonate, cyclohexyl vinyl ether, etc. are mentioned. As a compound which has two or more vinyl ether radicals, the cyclohexane dimethanol divinyl ether, triethylene glycol divinyl ether, the novolak mold divinyl ether, etc. are mentioned. In this case, as the blending ratio of coal of a compound which has a vinyl ether radical, 5 - 95 weight section is desirable to the total quantity 100 weight section of the compound which has the 1-4 above-mentioned oxetane rings, and the compound which has a vinyl ether radical.

[0058] The 4th invention of this invention is a constituent for precoat steel plate manufacture containing the compound and the optical radical polymerization initiator which have an acryloyl radical further (meta) in the constituent of the 1st invention. In this case, adjustment of constituent viscosity and reforming of the hardening film degree of hardness of a constituent can be performed by making the compound which has an acryloyl (meta) radical contain in a constituent. (Meta) Various things can be used as a compound which has an acryloyl radical. For example, as a compound which has one acryloyl (meta) radical, the acrylate (meta) of the alkylene oxide addition product of these alcohol etc. is mentioned to the acrylate (meta) of a phenol, nonyl phenol, and 2-ethylhexanol, and a list. (Meta) As a compound which has two acryloyl radicals, the di(meth)acrylate of the alkylene oxide addition product of these alcohol etc. is mentioned to the di(meth)acrylate of bisphenol A, isocyanuric acid, ethylene glycol, and propylene glycol, and a list. (Meta) As a compound which has three acryloyl radicals, the Tori (meta) acrylate of the alkylene oxide addition product of these alcohol etc. is in pentaerythritol, trimethylol propane and the Tori (meta) acrylate of isocyanuric acid, and a list, and the Pori (meta) acrylate of pentaerythritol and dipentaerythritol etc. is mentioned as a compound which has four or more acryloyl (meta) radicals. Moreover, acrylic monomer oligomer with conventionally well-known the

urethane acrylate which uses a urethane bond as a principal chain, the polyester acrylate which uses an ester bond as a principal chain, the epoxy (meta) acrylate which added the acrylic acid to the epoxy compound etc. is mentioned. In this case, as the blending ratio of coal of a compound which has an acryloyl (meta) radical, 5 - 95 weight section is desirable to the total quantity 100 weight section of the compound which has the 1-4 above-mentioned oxetane rings, and the compound which has an acryloyl (meta) radical. An optical radical polymerization initiator is blended with a constituent in the 4th invention of this invention. Various things can be used as an optical radical polymerization initiator. As a desirable thing A benzophenone and its derivative, benzoin alkyl ether, 2-methyl [4-(methylthio) phenyl]-2-morpholino-1-propanone, Benzyl dimethyl ketal, 1-hydroxy cyclohexyl phenyl ketone, 2-hydroxy - 2-methyl-1-phenyl propane-1-ON, alkyl phenylglyoxylate, a diethoxy acetophenone and 2-benzyl-2-dimethylamino-1-(4-morpholino phenyl)-1-butane -- non, acyl phosphine oxide etc. is mentioned to a list. As for the content of these optical radical polymerization initiators, it is desirable that it is 0.01 - 20 % of the weight to the compound which has an acryloyl (meta) radical.

[0059] Moreover, in this invention, two or more sorts chosen as the compound which has the epoxy group described above to the constituent of the 1st invention, and the compound list which has a vinyl ether radical from [(meta) the compound and the optical radical polymerization initiator] which have an acryloyl radical can also be blended. In this case, it is desirable that the total quantity of the compound which has the compound which has an epoxy group, the compound which has a vinyl ether radical, and (meta) an acryloyl radical to the total quantity 100 weight section of a compound which has the compound which has the 1-4 above-mentioned oxetane rings, the compound which has an epoxy group, the compound which has a vinyl ether radical, and (meta) an acryloyl radical as these blending ratio of coal is 5 - 95 weight section.

[0060] Inerts like an inorganic bulking agent, a color, a pigment, a viscosity modifier, a processing agent, an organic solvent, and an ultraviolet-rays cutoff agent can be blended with the constituent of this invention in the amount to the 100 weight sections per hardenability component of the 100 weight sections besides the above-mentioned component.

[0061] The photosensitizer other than an optical cationic initiator or/and an optical radical polymerization initiator can be added to the constituent of this invention, and the wavelength of UV field can also be adjusted to it. as the typical sensitizer which can be used in this invention -- Crivello -- what [J.V.Crivello, Adv.in Polymer Sci., 62, and 1 (1984)] are indicating is mentioned, and, specifically, there are a pyrene, perylene, an acridine orange, a thioxan ton, 2-chloro thioxan ton, a benzoflavin, etc.

[0062] O As a steel plate which can apply the constituent of steel plate this invention, a cutting plate or a coiled form griddle, hot rolled sheet steel, cold rolled sheet steel, an alloy galvanized steel sheet, an electro-galvanizing steel plate, a fused salt galvanized steel sheet or the thing to which chemical conversion, such as a chromic acid and phosphating, was performed at these, an aluminum plate, a stainless plate, a tin plate, a CHINFURI steel plate, etc. can be mentioned. In a steel plate, you may pretreat if needed. In using what is the production process and already performed chemical conversion, as described above, what is not performing chemical conversion should just perform pretreatment according to the quality of the material that what is necessary is just to only perform washing processing. Moreover, as a steel plate, that to which the primer was applied on the surface of the steel plate can also be used. By applying a primer on the surface of a steel plate, the corrosion-resistance of a precoat steel plate, adhesion with a constituent, etc. are improvable. As a primer, various things can be used, for example, an epoxy resin, a modified epoxy resin, a bisphenol, epoxy acrylate, polyester, etc. are mentioned.

[0063] O What is necessary is just to make it harden by the exposure of an activity energy line, after applying the constituent of this invention to a steel plate according to conventional methods, such as direct paint and printing, as the manufacture approach of the precoat steel plate which uses the constituent of manufacture approach this invention of a precoat steel plate. In painting directly, there is the approach of a curtain flow coat, a roll coat, a spray coat, etc., and when applying by printing, the usual printing approach by the offset method, the gravure offset method, an offset method, etc. can be used. Moreover, when quality of a low boiling material, such as a solvent, is added in a constituent, this

is evaporated before irradiating an activity energy line. In this case, it is made to usually evaporate with heating and a heating furnace, a far-infrared furnace, or a super-far-infrared furnace can be used as that approach. As an activity energy line, ultraviolet rays, an X-ray, an electron ray, etc. are mentioned. Various things can be used as the light source which can be used when making it harden by ultraviolet rays, for example, a mercury arc lamp, a xenon arc lamp, a fluorescent lamp, a carbon arc lamp, a tungsten-halogen copy lamp, etc. are mentioned. Although it is made to usually harden with the electron ray of energy 300eV or less when making it harden with an electron ray, it is possible to also make it harden with the exposure of 1Mrad - 5Mrad in an instant. Since cheap equipment can be used in this invention, it is desirable to use ultraviolet rays for hardening of a constituent.

[0064] The coating of further others etc. can also be applied to the precoat steel plate obtained by the invention in this application on this front face.

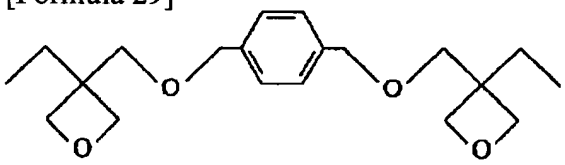
[0065]

[Example] An example and the example of a comparison are given to below, and this invention is explained more concretely. In addition, the section in each following example is weight criteria.

[0066] Stirring mixing of the following compound (30) (henceforth Component G) 4 section was carried out as the following compound (29) (henceforth Component A) 100 section which has the manufacture oxetane ring of an example 1- constituent and which has the two following oxetane rings as a compound, and an optical cationic initiator, and the constituent for precoat steel plate manufacture was manufactured.

[0067]

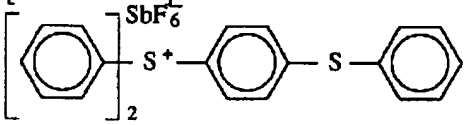
[Formula 29]



(29)

[0068]

[Formula 30]



(30)

[0069] - coating of the manufacture profit **** constituent of a precoat steel plate was carried out by the thickness of 10 micrometers on the BONDE light steel plate of the thickness of 0.8mm, width of face of 50mm, and the magnitude of die-length ** of 150mm, this is repeated on condition that conveyor speed 10 m/min in under the high-pressure mercury lamp of 80 W/cm and a condensing mold to 10cm location, the bottom of a mercury lamp was passed, and it was made to harden The following evaluations were performed about the constituent and hardening film which were obtained. The result is shown in the following table 2.

[0070] O The count of pass (count of passage) until adhesiveness disappears from a front face on the hardenability above-mentioned hardening conditions estimated.

[0071] O a pencil -- ****** -- having had -- the hardening film -- JISK It evaluated according to 5400.

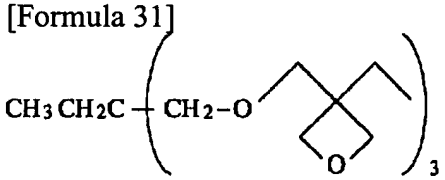
[0072] O the adhesion profit **** hardening film -- 1mm spacing -- the squares -- slitting -- putting in -- JISK Adhesion was evaluated according to 5400. In addition, O in Table 2, **, and x show following semantics.

O : [0073] which separates exceeding x:50% which almost remains peeling-less **:50% or more O on the E. I. du Pont de Nemours impact profit **** hardening film, the 1kg weight was dropped from height of 30cm, and an impact was given. The crack of the paint film side which this produced, exfoliation, etc. were evaluated with the naked eye. In addition, O in Table 2, **, and x show following semantics.

O : a crack, x:crack which **:crack exfoliation is not accepted to be produces for a while, [0074] in which exfoliation is accepted O 0T impact folding profit **** hardening film surface was ****ed outside, and was bent 180 degrees, and the naked eye estimated the crack of the produced paint film side etc. In addition, O in Table 2, **, and x show following semantics.
O : [0075] which a crack produces and x:crack which **:crack which is not produces slightly produces The constituent was manufactured like the example 1 except having used the component of the presentation shown in two to example 7 table 1. The precoat steel plate was manufactured like the example 1 using the obtained constituent. About the obtained hardening film, it evaluated like the example 1. Those results are shown in Table 2.
[0076] The constituent was manufactured like the example 1 except having used the component of the presentation shown in one to example of comparison 3 table 1. The precoat steel plate was manufactured like the example 1 using the obtained constituent. About the obtained hardening film, it evaluated like the example 1. Those results are shown in Table 2.
[0077]
[Table 1]

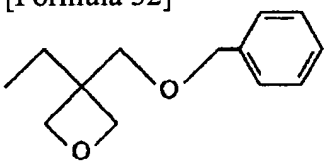
	A	B	C	D	E	F	G	H
実施例1	100						4	
実施例2	50	50					4	
実施例3			25		75		4	
実施例4	75					25	3	1
実施例5	25			50		25	3	1
実施例6	50				25	25	3	1
実施例7	75			25			4	
比較例1					100		4	
比較例2				25		75	1	3
比較例3					75	25	3	1

[0078] In Table 1, several show the section each. Moreover, in Table 1, component B-H shows the following compounds.
[0079] - Component B (compound which has three oxetane rings)
[0080]
[Formula 31]



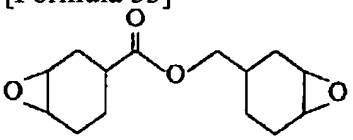
(31)

[0081] - Component C (compound which has one oxetane ring)
[0082]
[Formula 32]



(32)

[0083] - Component D (compound which has two epoxy groups)
[0084]
[Formula 33]



(33)

[0085] - Component E (compound which has two vinyl ether radicals)
[0086]
[Formula 34]

$$CH_2=CH-O-(CH_2CH_2O)_3CH=CH_2 \qquad (34)$$

[0087] - Component F (compound which has two acryloyl radicals)
[0088]
[Formula 35]

$$CH_2=\underset{\underset{O}{\|}}{CHCO}-(CH_2)_6-\underset{\underset{O}{\|}}{OCCH}=CH_2 \qquad (35)$$

[0089] - Component H (optical radical polymerization initiator)
[0090]
[Formula 36]

$$Ph-\underset{\underset{O}{\|}}{C}-\overset{\overset{O\ CH_3}{|}}{\underset{\underset{O\ CH_3}{|}}{C}}-Ph \qquad (36)$$

[0091]
[Table 2]

	硬化性(ﾊﾟｽ)	鉛筆硬度	密着性	デュポン衝撃	0T衝撃折曲げ
実施例1	7	3H	○	○	○
実施例2	6	4H	○	○	○
実施例3	3	H	○	○	○
実施例4	6	3H	○	○	○
実施例5	2	2H	○	△	○
実施例6	3	H	○	○	△
実施例7	2	3H	○	○	○
比較例1	3	F	○	△	△
比較例2	11	2H	×	×	△
比較例3	8	H	○	△	×

[0092]
[Effect of the Invention] The constituent for precoat steel plate manufacture of this invention has a quick cure rate, and the hardening film can use it for a degree of hardness, shock resistance, the adhesion, a steel plate, and the manufacture that it bends 0T, excels in workability, and are various precoat steel plates.

[Translation done.]